

UDC 666.112.2:666.122.2:532.73

GENERALIZED UNIVERSAL CALCULATION OF SiO₂ DIFFUSION COEFFICIENTS IN MELTS OF THE Na₂O – SiO₂ SYSTEM

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Experimental data are summarized, and a generalized formula for the calculation of SiO₂ diffusion coefficients in melts of the Na₂O – SiO₂ system is obtained. The formula is recommended for the practical calculations of the process of melting impure sodium disilicate.

The values of SiO₂ diffusion coefficients in melts of the Na₂O – SiO₂ system have been experimentally determined only for occasional compositions and temperatures. The lack of reference data on this important kinetic characteristic in the literature substantially impedes practical calculations of glass-melting processes for soluble sodium silicate glass.

A set of diffusion coefficients values required for generalization has been obtained by us using the calculation method based on kinetic curves of the dissolution of SiO₂ grains in glass melt [1] and experimental data [2] on the effect of temperature on the rate of batch melting of sodium silicate glasses listed in Table 1.

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TABLE 1

Batch silica modulus	Duration of sodium silicate melting, * sec, at melting temperature, °C			
	1450	1500	1550	1600
2.6	740	525	330	190
3.0	1140	890	510	300
3.5	1660	1230	700	435

* Initial size of sand grains in the batch 0.417 mm.

TABLE 2

Batch silica modulus	Estimated modulus of melt*	Coefficients of SiO ₂ diffusion, 10 ^{–12} m ² /sec, at melting temperature, °C			
		1450	1500	1550	1600
2.6	2.48	18.77	23.57	33.03	48.11
3.0	2.86	14.70	16.49	24.80	34.46
3.5	3.34	12.76	14.66	21.57	27.60

* Modulus of the melt at the estimated point of the kinetic curve of the dissolution of SiO₂ grains [1].

For each melting regime listed in [2] the respective values of SiO₂ diffusion coefficients were calculated (Table 2).

The obtained data array of diffusion coefficients can be mathematically described by the power dependence of the following form:

$$D = k M^n,$$

where M is the silica modulus of the melt; k and n are the equation parameters depending on temperature.

Based on numerical values of this parameter listed in Table 3, their functional dependences on temperature have been established (Fig. 1):

$$k = \exp(-3.139 \times 10^4 T^{-1} - 5.346);$$

$$n = 1.185 \times 10^4 T^{-1} - 8.211.$$

The parameters of the generalized universal formula can be written in a more convenient form for practical applications as follows:

$$k = \exp(9.738t \times 10^{-3} - 37.669);$$

$$n = 3.966 - 3.659t \times 10^{-3}.$$

The temperature dependences of SiO₂ diffusion coefficients calculated on the basis of the generalized formula are

TABLE 3

Melting temperature, °C	10 ⁴ T ^{–1} , K ^{–1}	Parameters of equation $D = k M^n$		
		10 ¹¹ k	ln k	n
1450	5.804	5.96	–23.54	–1.294
1500	5.640	9.53	–23.07	–1.587
1550	5.485	15.77	–22.57	–1.710
1600	5.339	25.54	–22.09	–1.863

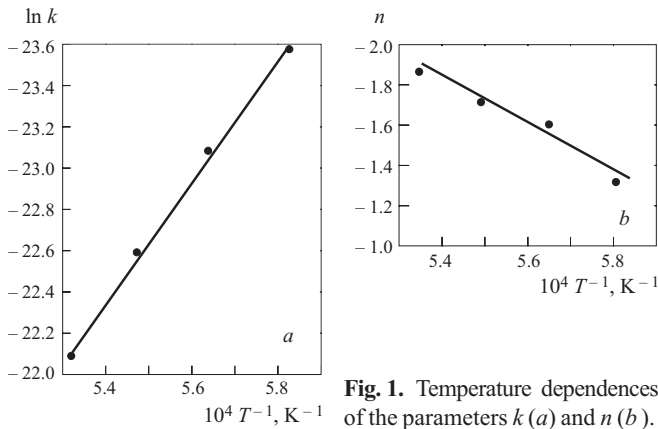


Fig. 1. Temperature dependences of the parameters k (a) and n (b).

correlated in Fig. 2 with experimental data known from the reference literature.

As the relation between the diffusion coefficients and temperature (similarly to the relation between the viscosity coefficients of glass melts and temperature) is expressed by the exponential law, this dependence in the coordinates $\ln D - T^{-1}$ is represented by a straight line, whose tangent is equal to the diffusion activation energy value.

The estimated temperature dependences (Fig. 2, curve 1) agree well with the data in [3] (curve 2): the dependences given for the melt with $M=2.0$ have the identical form. However, as the dissolution of vitreous silica in the melt was studied in the conditions of free convection, curve 2 naturally corresponds to slightly higher values of the diffusion coefficients.

A significant (by an order of magnitude) discrepancy is observed in the correlation with curve 3 reflecting the data on SiO₂ diffusion in sodium silicate melt with the modulus $M=3.535$ [4].

These data were obtained by mathematical processing of the results of electron microprobe measurements of thicknesses of the boundary diffusion layers h formed around quartz sand grains in the course of their dissolution in the melt.

The SiO₂ diffusion coefficients in this case were found from the following equation:

$$D = h A_D \exp\left(-\frac{E_D}{RT}\right). \quad (1)$$

However, the reliability of the diffusion coefficients based on this equation to a large extent depends on the degree of consistency of the real melting conditions with the frequency factor A_D and diffusion activation energy E_D that make part of the equation. The authors in their calculations used the following values of these parameters:

$$A_D = 9.256 \times 10^{-3} \text{ sec}^{-1};$$

$$E_D = 72.68 \times 10^3 \text{ J/mole (17.37 kcal/mole)}.$$

The specified discrepancy could be also caused by the fact that in measuring the thickness of diffusion boundary

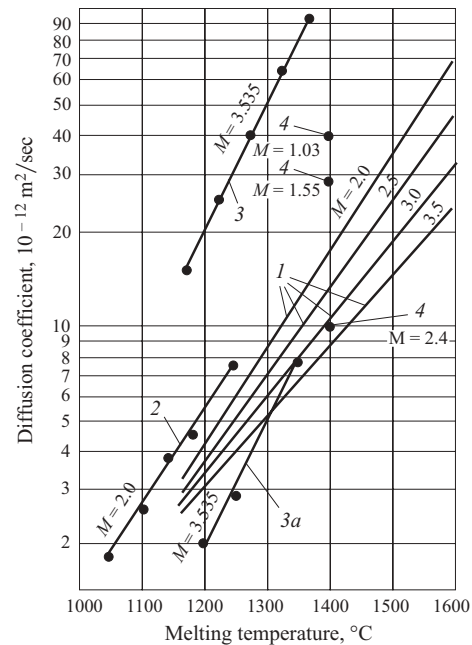


Fig. 2. Temperature dependences of the coefficient of diffusion SiO₂ in melts of the Na₂O – SiO₂ system: 1) calculated based on the generalized formula; 2 and 3) experimental data from [3] and [4], respectively; 3a) calculation based on experimental data from [4] and [5]; 4) experimental data from [6].

layers, which make part of Eq. (1), their arbitrarily defined boundaries may be not quite accurate.

The analysis performed by us taking into account the experimental data on the dissolution kinetics of quartz sand grains in the melt of the same chemical composition [5] made it possible to propose a different approach to processing the results of the measurements of diffusion boundary layers and a different formula for the calculation of SiO₂ diffusion coefficients.

The essence of the method proposed is as follows.

For the quantitative estimate of the resultant constant K_v of the velocity of the heterogeneous process of the dissolution of SiO₂ particles, whose values for sodium silicate melt with $M=3.535$ in the temperature interval of 1050 – 1350°C were determined in [5], a classical expression is known:

$$K_v = \frac{K_s D / h}{K_s + D / h}, \quad (2)$$

where K_s is the constant of the chemical reaction velocity on the reaction surface, m/sec; $\frac{D}{h} = A_D \exp\left(-\frac{E_D}{RT}\right)$ is the constant of the diffusion mass transfer velocity, m/sec.

For the sodium silicate melt considered the authors in [5] also established that within the temperature interval of 1150 – 1170°C the dissolution process passes from the ki-

TABLE 4

Melting temperature, °C	Diffusion layer thickness, 10^{-9} m*	Dissolution rate constant, 10^{-6} m/sec**	Diffusion coefficient, 10^{-12} m ² /sec
1050	—	6.4	—
1100	—	12.3	—
1150	—	20.2	—
1175	65.50	—	—
1200	78.44***	24.3	1.906
1225	93.00	—	—
1250	110.95***	26.1	2.896
1275	122.50	—	—
1300	143.45***	35.6	5.107
1325	161.00	—	—
1350	175.94***	43.1	7.583
1375	194.00	—	—

* Based on data from [5].

** Based on data from [6].

*** Estimated values determined by interpolation based on the experimental dependence $d = f(t)$ [4].

netic range into the diffusion range, for which the following relation holds:

$$K_s = \frac{D}{h}.$$

Taking into account this relation, expression (2) takes the form:

$$K_v = \frac{D}{h}$$

and, accordingly, the formula for the calculation of diffusion coefficients is:

$$D = hK_v.$$

The results of our calculations of diffusion coefficients of SiO₂ in the sodium silicate melt with $M = 3.535$ are listed in Table 4, and the temperature dependence in Fig. 2 is represented by curve 3a.

It can be seen that the diffusion coefficient values on curve 3a agree well with the values calculated using the generalized formula.

The reliability of the values of SiO₂ diffusion coefficients calculated on the basis of the generalized formula for melts of the Na₂O – SiO₂ system is also confirmed by the data in [6], which are shown in Fig. 2 as dots 4.

The established agreement between the diffusion coefficient values calculated based on the generalized universal formula and the experimental data obtained by different researchers provides reason enough to recommend this formula for application in practical calculations of melting impure sodium disilicate.

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